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THE ENERGY OF THE VITREOUS LATTICE OF AMORPHOUS SILICA

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The concept of energy of a vitreous lattice is considered, its meaning is discussed, and a quantitative evaluation of this parameter with respect to quartz glass is carried out.

The concept of “crystal lattice energy” E_{lat} is well known for crystalline bodies and is understood as the work needed to fully overcome the interaction between the lattice points (atoms, ions, molecules, etc.) and bring them apart from each other to a distance at which the interaction force is equal to zero. Numerically this work is equal to the overall potential interaction energy of all lattice points per mole of material (for SiO_2 $E_{\text{lat}} = 1776.56$ kJ/mole). An attempt was made in [1] to introduce the concept of the “energy of a vitreous lattice.” The present study considers this problem in more detail.

When a crystal is being heated and melted in quasistatic conditions, the energy of the oscillatory motion of the lattice points keeps increasing, the thermal defects gradually accumulate, and the geometry (syngony) of the lattice is modified (in the case of polymorphous transformations), which is accompanied by fine effects in the character of the chemical bond. At a temperature close to the melting point and in the course of melting, the torsional-rotational motion of the silicon-oxygen tetrahedra intensifies, which leads to a modification of the angle of the Si–O–Si bond. Furthermore, in systems with a complex chemical composition, the translational motion (diffusion) of the modifier ions in the system volume increases with increasing temperature. A certain amount of energy is spent on this (ΔH positive), and the initial level of the potential interaction energy of the lattice points of the crystalline material or the melt decreases.

In the vitrification of a melt (a metastable nonequilibrium process), crystallization does not occur, and the emerging glass accumulates part of ΔH , which suggests that glass is a less thermodynamically stable phase than the initial crystal. The overall potential interaction energy of all nodes of a vitreous lattice (i.e., a spatially disordered structure of glass as distinct from an ordered crystal lattice) per mole of material can be appropriately termed the energy of the vitreous lattice E_{vlat} .

Let us consider an equilibrium regime of heating and melting of crystalline silica, when theoretically the structural

relaxation in the silicate corresponds to the temperature variations within the system, i.e., the rate of heating is very low (Fig. 1). At a temperature of 848 K, the initial β -quartz rather quickly transforms into α -quartz, which is accompanied by an insignificant thermal effect ($\Delta H_1 = 0.628$ kJ/mole) [2]. Next α -quartz, in its turn, according to the Flerke scheme at a temperature of about 1673 K, slowly transforms (with an endothermic effect of $\Delta H_2 = 0.838$ kJ/mole) into high-temperature α -cristobalite, which melts at a temperature of about 2000 K. The melting enthalpy ΔH_m varies from 7.704 to 9.210 kJ/mole [2, 3]. The melt of SiO_2 exists at a temperature over 2000 K.

In Fig. 1 the equilibrium process of heating and melting of SiO_2 is indicated by a complicated line 1–2–3–4–5–6–7–8. The overall enthalpy increment in this case (at point 7) amounts to

$$\Delta H = \int_{298}^{848} C_{\beta\text{-q}} dT + \Delta H_1 + \int_{848}^{1673} C_{\alpha\text{-q}} dT + \Delta H_2 + \int_{1673}^{2000} C_{\alpha\text{-cr}} dT + \Delta H_m. \quad (1)$$

The values ΔH_1 , ΔH_2 , and ΔH_m correspond to the heat (enthalpy) of the respective phase transformations. Components of the type $\int C dT$ in Eq. (1) are continuous within the respective temperature intervals and, on the whole, increase with increasing temperature. The heat capacity can be represented by the sum

$$C = C_{\text{osc}} + C_{\text{dif}} + C_{\text{def}} + C_r, \quad (2)$$

where C_{osc} , C_{dif} , and C_r are the heat capacity components responsible for the contributions made by the oscillatory, translational (diffusion), and rotational (torsional-rotational) forms of motion of the crystal elements to the increment of the enthalpy of SiO_2 ; C_{def} is the heat capacity component related to the formation of thermal defects in the structure of SiO_2 (for instance, thermal rupture of –Si–O–Si– bonds).

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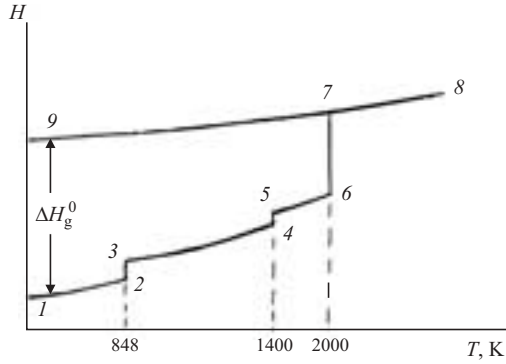


Fig. 1. Enthalpy variation in heating and melting of crystalline SiO_2 and vitrification of the melt.

In certain systems (metals), other components are possible as well in Eq. (2), in particular, the components related to electrons breaking away from the outer atom shells and ion shells and migrating in the volume of the system. In an ideally pure SiO_2 , which is a good dielectric, this component is equal to zero. One can also neglect the magnitude of C_{dif} , as this component is caused by the presence of impurity modifier ions, and such ions in the ideal case do not exist in pure SiO_2 .

The oscillation amplitude of Si and O particles and $[\text{SiO}_4]$ tetrahedra vary little with increasing temperature, which is evidenced by the low values of the CTLE of silica in a wide temperature range. Therefore, it can be accepted that C_{osc} depends but little on the temperature and is an almost constant value within a wide temperature interval. It is apparently appropriate to take the standard value of the heat capacity of silica at a temperature of 298 K as C_{osc} , especially since these values virtually coincide for the main silica forms; $C_{\beta\text{-q}}^0 = 44.46 \pm 0.1 \text{ J/(mole} \cdot \text{K)}$; $C_{\alpha\text{-cr}}^0 = 44.21 \pm 0.01 \text{ J/(mole} \cdot \text{K)}$; $C_{\text{q.g}}^0$ (quartz glass) = $44.41 \text{ J/(mole} \cdot \text{K)}$ [2].

With growing oscillation amplitude of the lattice points, the rigid polymer structure of SiO_2 is loosened and, as the temperature increases, the number of broken Si – O – Si bonds in SiO_2 (i.e., the number of uncoupled orbitals) grows. Before a certain quantity of such ruptures is accumulated, torsional-rotational motion in the rigidly bonded tetrahedrons $[\text{SiO}_4]$ is little probable.

To rupture a single bond of Si – O, one should spend an amount of energy that in the first approximation is equal to the energy of a single bond,

$$\varepsilon_{\text{Si-O}} = \frac{444.14}{6.02 \times 10^{23}} = 7.38 \times 10^{-19} \text{ J/bond},$$

where 444.14 kJ/mole is the molar energy of the Si – O bond [4].

If at a certain temperature, n ruptures have occurred, the increase in the enthalpy of SiO_2 will be equal to

$$\Delta H_{\text{def}} = n\varepsilon_{\text{Si-O}}.$$

The value ε in covalent systems does not depend on the long-range order (in the second and third coordination

spheres); therefore the value $\varepsilon_{\text{Si-O}}$ can be regarded as a constant in a wide temperature interval.

Assuming that the formation of the defects mentioned (thermal ruptures of bonds) proceeds in an equilibrium regime, the variation of the isobaric-isothermic potential of the crystal in defect formation will amount to

$$\Delta G = \Delta H_{\text{def}} - T\Delta S = n\varepsilon_{\text{Si-O}} - T\Delta S,$$

where ΔS is the increment in the entropy of the system in defect formation.

Applying the classical principles of thermodynamics of equilibrium processes and taking into account the Boltzmann – Planck formula and the Stirling approximation, one obtains the expression

$$\ln \frac{n}{N-n} \approx \frac{\varepsilon_{\text{Si-O}}}{kT} \quad \text{or} \quad \frac{n}{N-n} \approx e^{-\varepsilon_{\text{Si-O}}/kT},$$

where N is the total number of Si – O chemical bonds per mole of material; n is the equilibrium number of thermally broken Si – O bonds per mole of material at a certain temperature T ; and k is the Boltzmann constant.

With $n \ll N$, we can take $N - n \approx N$, then

$$\frac{n}{N} = e^{-\varepsilon_{\text{Si-O}}/kT} \quad \text{or} \quad n = Ne^{-\varepsilon_{\text{Si-O}}/kT}. \quad (3)$$

Hence

$$\Delta H_{\text{def}} = \varepsilon_{\text{Si-O}} Ne^{-\varepsilon_{\text{Si-O}}/kT};$$

$$C_{\text{def}} = \frac{d(\Delta H_{\text{def}})}{dT}.$$

Thus, the number of thermally ruptured Si – O bonds in silica grows exponentially with increasing temperature (in equilibrium quasistatic heating).

On reaching the melting point the SiO system has a sufficient level of bond ruptures for the crystalline lattice to become unstable and transform into a melt. In the case of equilibrium, $T_m = \text{const}$. This means that the amplitude of thermal oscillations of the system points remains constant and the number of thermal ruptures of Si – O bonds accumulated at the moment of melting of the crystal does not grow and remains virtually constant (Formula (3)). Hence it follows that the main contribution to ΔH_m is made by disordering of the polymeric structure of SiO_2 , i.e., a perceptible intensification of the torsional-rotational motion of $[\text{SiO}_4]$ tetrahedra and a relatively fast modification of the angle of the Si – O – Si bond from 120 to 180°. As this does not lead to the rupture of bonds between the tetrahedra $[\text{SiO}_4]$, it is not surprising that the magnitude of ΔH_m is relatively low (7.704 – 9.210 kJ/mole).

Quartz glass is produced by nonequilibrium chilling of SiO_2 melt to low temperatures (line 7 – 9 in Fig. 1). With a fast decrease in the temperature, no mutually coordinated

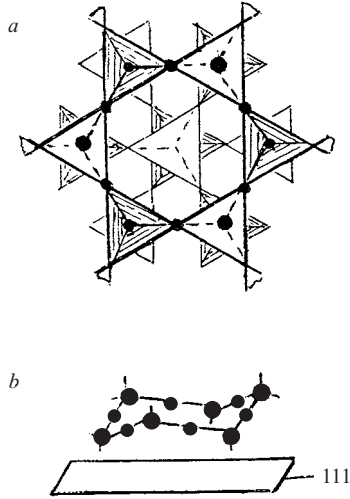


Fig. 2. A fragment of the structure of α -cristobalite: *a*) plane projection $\{111\}$; *b*) arrangement of silicon-oxygen loops with respect to plane $\{111\}$; \bullet) O particles; \blacksquare) Si particles.

turns of tetrahedra $[\text{SiO}_4]$ can occur in the polymer silicon-oxygen lattice, no crystallization is registered, and the amorphous lattice of the melt becomes “frozen” against the background of abruptly reduced thermal mobility of the structural elements of the melt. Thus, ΔH_m is accumulated by the glass, and ΔH_1 and ΔH_2 are absorbed as well. The presence of the “frozen” melt structure in glass makes it kinetically stable (i.e., a solid body), but thermodynamically unstable (compared with a crystal).

The thermal (mainly oscillatory) mobility of the structural elements of the silicon-oxygen lattice of quartz glass under the respective temperatures differs little from the thermal mobility in the crystalline silica lattice, since these materials have the same chemical composition, and the length and strength of the Si–O bond in them is virtually equal. This makes it possible to assert that

$$\int_{298}^{2000} C_{\text{osc}}^{\text{q-g}} dT \approx \int_{298}^{848} C_{\text{osc}}^{\beta\text{-q}} dT + \int_{848}^{1673} C_{\text{osc}}^{\alpha\text{-q}} dT + \int_{1673}^{2000} C_{\text{osc}}^{\alpha\text{-cr}} dT,$$

i.e., the energy spent on increasing the oscillation amplitude of the lattice points of the silicon-oxygen skeleton of crystalline silica up to the melting point is reversibly released in the ambient medium in vitrification. The part of the energy of $\int C dT$ components equal to $\int C_{\text{def}} dT$ (Eq. (1)) is divided into two parts: one part in restoring the thermally broken Si–O bonds in the course of cooling is as well released into the ambient medium in the form of heat, and the other part, equal to $n^* \epsilon_{\text{Si-O}}$, remains accumulated by the glass and enhances its excess enthalpy. The number n^* corresponds to the number of Si–O bonds remaining nonhealed (ruptured) Si–O in solidified glass (below the vitrification temperature T_g ; for quartz glass $T_g = 1473$ K). Since the process of vitrification

of a melt is metastable, $n^* > n$ (n is the thermodynamically equilibrium number of ruptures of Si–O bonds in crystalline silica at a certain temperature (Formula (3)). The dependence $n^* = f(T)$ is not known, since, apart from other factors, it is determined by the rate of cooling of the melt v_c :

$$\frac{dn^*}{d\tau} = \frac{dn^*}{dT} \frac{dT}{d\tau} = \frac{dn^*}{dT} v_0.$$

For quartz glass that solidifies very fast, this is not very significant, but in glasses with a complex chemical composition this dependence ought to be taken into account.

Thus, the total amount of the heat spent on changing the potential energy of crystalline silica in heating and melting, which correlates with the amount of energy accumulated by the glass, is equal to

$$\Delta H_g^0 = \Delta H_1 + \Delta H_2 + \Delta H_m + n^* \epsilon_{\text{Si-O}}.$$

According to the law of conservation of energy, the potential energy of the chemical bonds in SiO_2 decreases by the same magnitude in its transition from the crystalline state to the vitreous state, i.e.,

$$E_{\text{vlat}} = E_{\text{lat}} - (\Delta H_1 + \Delta H_2 + \Delta H_m + n^* \epsilon_{\text{Si-O}}).$$

The value of n^* is hard to estimate theoretically. Yet, based on the results of microelectrophoretic determination of the ξ -potential in extra-pure quartz glass and pure β -quartz, it is possible to estimate the number of thermally ruptured Si–O bonds per unit area of quartz glass surface. This value is about 0.8 bond per 1 nm^2 [5].

The number of all surface lattice points per 1 nm^2 of the quartz glass surface can be best estimated by analyzing the $\{111\}$ lattice of α -cristobalite, whose density is close to that of quartz glass. Figure 2*a* represents a fragment of the projection of α -cristobalite structure on plane $\{111\}$ in the form of hexagonal rings of $[\text{SiO}_4]$ tetrahedra. The fracture surface of SiO_2 is not smooth and resemble a “crimped” grid of tetrahedron rings (Fig. 2*b*). Therefore, in estimating the surface area of silica, one should not take the projection of the hexagonal ring on the $\{111\}$ plane but the surface area of a “crimped” ring, whose sides are equal to the length of a Si–O–Si bond ($0.162 \times 2 = 0.324 \text{ nm}$) and are slanted toward the $\{111\}$ plane. This surface area is equal to 0.2576 nm^2 . There are $1/0.2576 = 3.9$ rings per 1 nm^2 . The oxygen particles located on the sides of such rings simultaneously belong to two rings, whereas the silicon particles in the hollows of the lattice (nonhatched tetrahedra) and the oxygen particles in the protrusions of the lattice (hatched tetrahedra) simultaneously belong to all three tetrahedra.

Thus, the number of surface particles per one “crimped” loop is $6 \times \frac{1}{2} + 6 \times \frac{1}{3} = 5$, or $5 \times 3.9 = 19.5$ particles per 1 nm^2 . Assuming that there are statistically four Si–O bonds per three particles (1Si + 2O) of silica, the total number of

surface bonds is $(19.5/3) \times 4 = 25.2$ bonds per 1 nm^2 (taking into account the corrugated surface). Then the share of thermally ruptured Si – O bonds in quartz glass (n^*/N) will be equal to $0.8/25.2 \approx 0.03$, i.e., 3%. The same share of E_{lat} will be accumulated by the glass:

$$n^* \varepsilon_{\text{Si-O}} = 0.03 E_{\text{lat}} = 0.03 \times 1776.56 = 53.28 \text{ kJ/mole.}$$

In this case

$$\begin{aligned} \Delta H_{\text{g}}^0 &= \Delta H_1 + \Delta H_2 + \Delta H_{\text{m}} + n^* \varepsilon_{\text{Si-O}} = \\ &0.628 + 0.838 + 7.704 + 53.28 = 62.45 \text{ kJ/mole;} \end{aligned}$$

$$E_{\text{vlat}} = E_{\text{lat}} - \Delta H_{\text{g}}^0 = 1776.57 - 62.45 = 1714.11 \text{ kJ/mole.}$$

It follows from the calculation data that the main contribution to the excess enthalpy of glass ΔH_{g}^0 is contributed by the component of the inner energy spent on breaking Si – O bonds in the course of heating crystalline silica to the melting point and not on changing the system enthalpy in phase

transformations (ΔH_1 , ΔH_2 , and ΔH_{m}), as would be expected at a glance.

The decrease in the value of E_{vlat} (1714.11 kJ/mole) compared with E_{lat} (1776.57 kJ/mole) accounts for the deterioration of the strength properties, hardness, and chemical resistance of quartz glass compared with crystalline silica.

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